

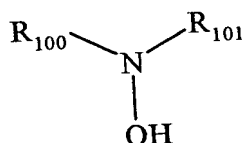
CLAIMS

What is claimed is:

1. A method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of at least one inhibitor that is a hydrogen donor or electron acceptor.

2. The method of claim 1 wherein the inhibitor is a hydrogen donor.

3. The method of claim 2 wherein the inhibitor is of the structure



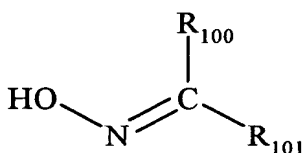
wherein

R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , $COOR_{102}$, $CONR_{102}R_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form

a ring structure of five to seven members.

4. The method of claim 2 wherein the inhibitor is of the structure

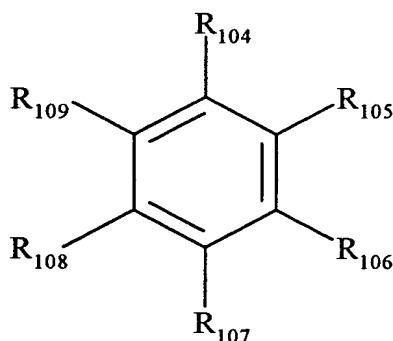


wherein

R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , COOR_{102} , $\text{CONR}_{102}\text{R}_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

5. The method of claim 2 wherein the inhibitor is of the structure



wherein

R₁₀₄, R₁₀₅, R₁₀₆, R₁₀₇, R₁₀₈, and R₁₀₉ are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR₁₁₀, NR₁₁₀R₁₁₁, SR₁₁₀, NO₂, NO, CN, COR₁₁₂, halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members, provided that at least one of R₁₀₄, R₁₀₅, R₁₀₆, R₁₀₇, R₁₀₈, and R₁₀₉ is OH or NHR₁₁₀;

R₁₁₀ and R₁₁₁ are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR₁₀₂, or R₁₁₀ and R₁₁₁ can be taken together to form a ring structure of five to seven members;

R₁₁₂ is R₁₀₂, OR₁₀₂, or NR₁₀₂R₁₀₃; and

R₁₀₂ and R₁₀₃ are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the

substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

6. The method of claim 5 wherein R_{104} is OH.

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7. The method of claim 6 wherein R_{107} is OH.

8. The method of claim 6 wherein R_{105} is OH.

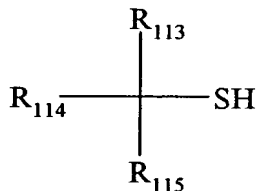
9. The method of claim 6 wherein at least one of R_{105} and R_{107} is NO_2 .

10. The method of claim 6 wherein at least one of R_{105} and R_{107} is NO.

11. The method of claim 5 wherein R_{104} is NHR_{110} and at least one of R_{105} and R_{107} is NO_2 .

12. The method of claim 5 wherein R_{104} is NHR_{110} , R_{107} is $NR_{110}R_{111}$, and R_{111} is phenyl.

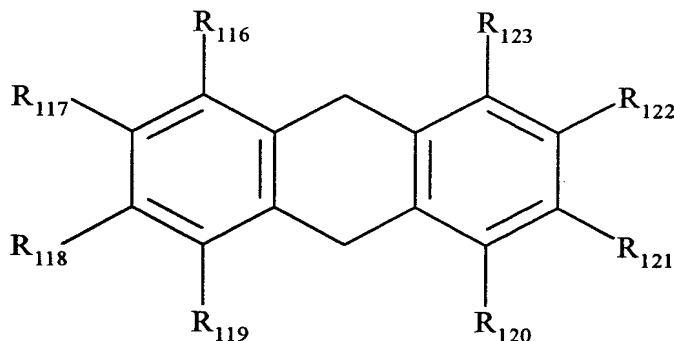
13. The method of claim 2 wherein the inhibitor is of the structure



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wherein R_{113} , R_{114} , and R_{115} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, and heterocyclic moieties.

14. The method of claim 2 wherein the inhibitor is of the structure



10

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wherein

R_{116} , R_{117} , R_{118} , R_{119} , R_{120} , R_{121} , R_{122} , and R_{123} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members;

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R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

5 R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

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15 15. The method of claim 2 wherein the inhibitor is selected from the group consisting of diethylhydroxylamine, cyclohexanoneoxime, dibenzylhydroxylamine, 2,4-dinitro-6-sec-butylphenol, N-phenyl-N'-(1,4-dimethylpentyl)-para-phenylenediamine, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone, methylhydroquinone, 4-t-butylhydroquinone, 4-t-butylcatechol, octanethiol, 2,6-di-t-butyl-4-ethylphenol/Cu(I)naphthenate, dihydroanthracene, N-t-butyl-2-benzothiazole-sulfenamide, and N-methyl-4-nitroaniline.

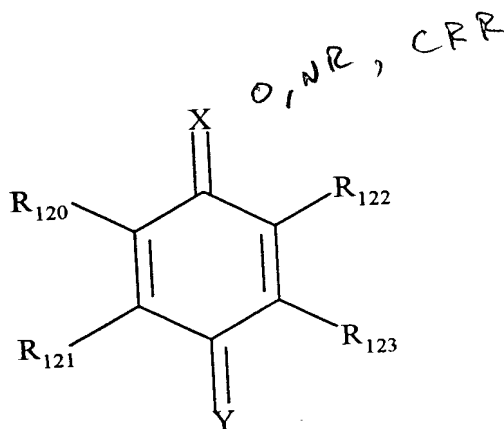
20 16. The method of claim 2 wherein a transition metal is added.

> 10w
p. 20, L 2+

17. The method of claim 16 wherein the transition metal is copper.

18. The method of claim 1 wherein the inhibitor is an electron acceptor.

19. The method of claim 18 wherein the inhibitor is of the structure



wherein

X and Y are independently selected from the group consisting of oxygen, NR_{110} , and $CR_{124}R_{125}$;

R_{120} , R_{121} , R_{122} , and R_{123} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO , NO_2 , CN , COR_{112} , and halogen, or R_{120} and R_{121} can be taken together and/or R_{122} and R_{123} can be taken together to form one or two ring structures, respectively, either of which can be of five to seven members;

R_{124} and R_{125} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or can be taken together

to form a ring structure of five to seven members,

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} , or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

20. The method of claim 19 wherein X and Y are oxygen.

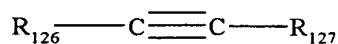
21. The method of claim 19 wherein X is oxygen and Y is $CR_{124}R_{125}$.

22. The method of claim 19 wherein X is oxygen and Y is NR_{110} .

23. The method of claim 19 wherein X and Y are NR_{110} .

24. The method of claim 21 wherein X is NR_{110} and Y is $CR_{124}R_{125}$.

25. The method of claim 18 wherein the inhibitor is of the structure



wherein

5 R_{126} and R_{127} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , and halogen,

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents
10 are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the
15 substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

26. The method of claim 18 wherein the inhibitor is selected from the group
consisting of phenylacetylene, 2,5-di-t-butyl-1,4-benzoquinone, 2,6-di-t-butyl-1,4-
20 benzoquinone, 1,4-benzoquinone, 2-methylanthraquinone, 1,4-naphthoquinone, 2,6-di-t-butyl-4-(phenylmethylene)-2,5-cyclohexadiene-1-one, 2,6-di-t-butyl-4-(phenylimino)-

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2,5-cyclohexadiene-1-one, and ethyl 3,4-bis-(3,5-di-t-butyl-4-one-2,5-cyclohexadienyldene)-hexane-1,6-dioate

27. The method of claim 18 wherein a transition metal is added.

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28. The method of claim 27 wherein the transition metal is copper..

29. The method of claim 1 wherein the inhibitor is a blend of a hydrogen donor and an electron acceptor.

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30. Method of claim 1 wherein said monomers contain impurities from the monomer production and/or purification processes.

31. Method of claim 30 wherein the impurities include polymer formed during the production and/or purification processes.

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32. Method of claim 31 wherein the polymer formed during the production and/or purification processes is soluble in the monomer stream.

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33. Method of claim 31 wherein the polymer formed during the production and/or purification processes is insoluble in the monomer stream.

34. Method of claim 1 wherein said monomers are undergoing purification by distillation.

35. Method of claim 34 wherein the distillation process occurs at pressures less than 760 mm Hg.

36. Method of claim 34 wherein the distillation process is a continuous process.

37. Method of claim 34 wherein the equipment in which the distillation process occurs contains polymer.

38. Method of claim 37 wherein the polymer was formed during the monomer's production and/or purification processes.

39. Method of claim 37 wherein the polymer is not dissolved in the monomer stream.

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40. Method of claim 34 wherein said monomers contain impurities from the monomer production and/or purification processes.

41. Method of claim 40 wherein the impurities include polymer formed during the production and/or purification processes.

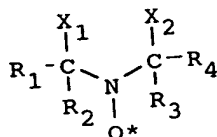
42. Method of claim 41 wherein the polymer formed during the production and/or purification processes is soluble in the monomer stream.

43. Method of claim 41 wherein the polymer formed during the production and/or purification processes is insoluble in the monomer stream.

44. A method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers

A) at least one first inhibitor that is a hydrogen donor or electron acceptor and

B) at least one second inhibitor having the following structural formula:



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wherein

R_1 and R_4 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl;

R_2 and R_3 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl; and

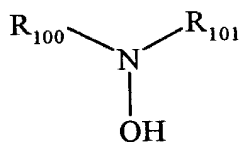
X_1 and X_2

(1) are independently selected from the group consisting of halogen, cyano, amido, -S- C_6H_5 , carbonyl, alkenyl, alkyl of 1 to 15 carbon atoms, $COOR_7$, -S-COR₇, and -OCOR₇, wherein R_7 is alkyl or aryl, or

(2) taken together, form a ring structure with the nitrogen.

45. The method of claim 44 wherein the first inhibitor is a hydrogen donor.

46. The method of claim 45 wherein the first inhibitor is of the structure



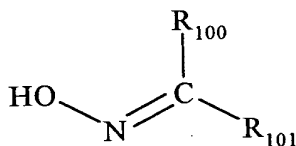
wherein

R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , $COOR_{102}$, $CONR_{102}R_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S,

or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

47. The method of claim 45 wherein the first inhibitor is of the structure

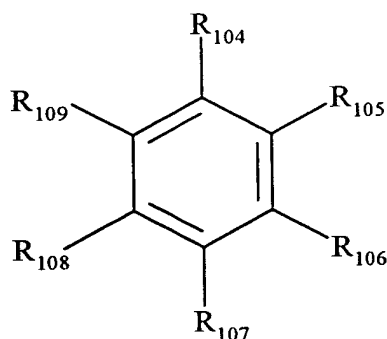


wherein

R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , $COOR_{102}$, $CONR_{102}R_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

48. The method of claim 45 wherein the first inhibitor is of the structure



wherein

R₁₀₄, R₁₀₅, R₁₀₆, R₁₀₇, R₁₀₈, and R₁₀₉ are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR₁₁₀, NR₁₁₀R₁₁₁, SR₁₁₀, NO₂, NO, CN, COR₁₁₂, halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members, provided that at least one of R₁₀₄, R₁₀₅, R₁₀₆, R₁₀₇, R₁₀₈, and R₁₀₉ is OH or NHR₁₁₀;

R₁₁₀ and R₁₁₁ are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR₁₀₂, or R₁₁₀ and R₁₁₁ can be taken together to form a ring structure of five to seven members;

R₁₁₂ is R₁₀₂, OR₁₀₂, or NR₁₀₂R₁₀₃; and

R₁₀₂ and R₁₀₃ are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R₁₀₂ and R₁₀₃ can be taken together to form

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a ring structure of five to seven members.

49. The method of claim 48 wherein R_{104} is OH.

50. The method of claim 49 wherein R_{107} is OH.

51. The method of claim 49 wherein R_{105} is OH.

52. The method of claim 49 wherein at least one of R_{105} and R_{107} is NO_2 .

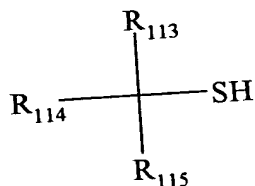
53. The method of claim 49 wherein at least one of R_{105} and R_{107} is NO.

54. The method of claim 48 wherein R_{104} is NHR_{110} and at least one of R_{105} and R_{107} is NO_2 .

55. The method of claim 48 wherein R_{104} is NHR_{110} , R_{107} is $NR_{110}R_{111}$, and R_{111} is phenyl.

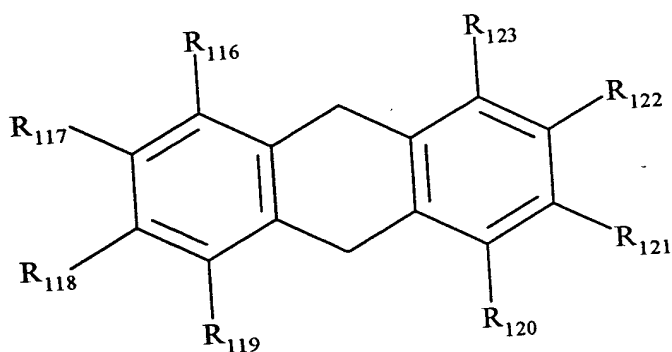
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56. The method of claim 45 wherein the first inhibitor is of the structure



wherein R₁₁₃, R₁₁₄, and R₁₁₅ are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, and heterocyclic moieties.

57. The method of claim 45 wherein the first inhibitor is of the structure



wherein

R₁₁₆, R₁₁₇, R₁₁₈, R₁₁₉, R₁₂₀, R₁₂₁, R₁₂₂, and R₁₂₃ are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR₁₁₀, NR₁₁₀R₁₁₁, SR₁₁₀, NO₂, NO, CN, COR₁₁₂, halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members;

R₁₁₀ and R₁₁₁ are independently selected from the group consisting of hydrogen, alkyl,

aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $\text{NR}_{102}\text{R}_{103}$; and

5 R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

10 58. The method of claim 45 wherein the first inhibitor is selected from the group consisting of diethylhydroxylamine, cyclohexanoneoxime, dibenzylhydroxylamine, 2,4-dinitro-6-sec-butylphenol, N-phenyl-N'-(1,4-dimethylpentyl)-para-phenylenediamine, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone, methylhydroquinone, 4-t-butylhydroquinone, 4-t-butylcatechol, octanethiol, 2,6-di-t-butyl-4-ethylphenol/Cu(I)naphthenate, dihydroanthracene, N-t-butyl-2-benzothiazole-sulfenamide, and N-methyl-4-nitroaniline.

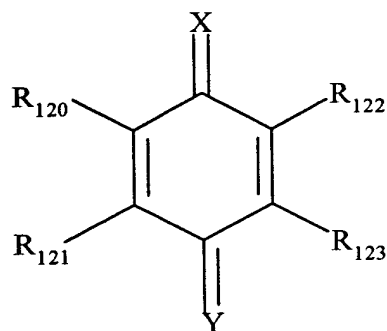
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59. The method of claim 45 wherein a transition metal is added.

20 60. The method of claim 59 wherein the transition metal is copper.

61. The method of claim 44 wherein the first inhibitor is an electron acceptor.

62. The method of claim 61 wherein the first inhibitor is of the structure



wherein

X and Y are independently selected from the group consisting of oxygen, NR_{110} , and $\text{CR}_{124}\text{R}_{125}$;

R_{120} , R_{121} , R_{122} , and R_{123} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $\text{NR}_{110}\text{R}_{111}$, SR_{110} , NO , NO_2 , CN , COR_{112} , and halogen, or R_{120} and R_{121} can be taken together and/or R_{122} and R_{123} can be taken together to form one or two ring structures, respectively, either of which can be of five to seven members;

R_{124} and R_{125} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $\text{NR}_{110}\text{R}_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or can be taken together

to form a ring structure of five to seven members;

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} , or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

63. The method of claim 62 wherein X and Y are oxygen.

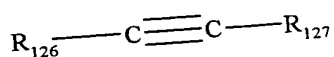
64. The method of claim 62 wherein X is oxygen and Y is $CR_{124}R_{125}$.

65. The method of claim 62 wherein X is oxygen and Y is NR_{110} .

66. The method of claim 62 wherein X and Y are NR_{110} .

67. The method of claim 62 wherein X is NR_{110} and Y is $CR_{124}R_{125}$.

68. The method of claim 55 wherein the inhibitor is of the structure



wherein

R_{126} and R_{127} are independently selected from the group consisting of hydrogen, alkyl,

aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} ,

$NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , and halogen,

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl,

aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents

are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form

a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl,

aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the

substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form

a ring structure of five to seven members.

69. The method of claim 61 wherein the first inhibitor is selected from the group

consisting of phenylacetylene, 2,5-di-t-butyl-1,4-benzoquinone, 2,6-di-t-butyl-1,4-

benzoquinone, 1,4-benzoquinone, 2-methylantraquinone, 1,4-naphthoquinone, 2,6-di-

t-butyl-4-(phenylmethylene)-2,5-cyclohexadiene-1-one, 2,6-di-t-butyl-4-(phenylimino)-

2,5-cyclohexadiene-1-one, and ethyl 3,4-bis-(3,5-di-t-butyl-4-one-2,5-

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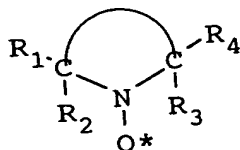
cyclohexadienyldene)-hexane-1,6-dioate.

70. The method of claim 61 wherein a transition metal is added.

71. The method of claim 70 wherein the transition metal is copper.

72. The method of claim 44 wherein the first inhibitor is a blend of a hydrogen donor and an electron acceptor.

73. The method of claim 44 wherein the second inhibitor is of the structure



wherein R₁ and R₄ are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R₂ and R₃ are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl, and the

portion represents the atoms necessary to form a five-, six-, or seven-membered

heterocyclic ring.

74. The method of claim 44 wherein the second inhibitor is a blend of two nitroxyls.

5 75. The method of claim 73 wherein the second inhibitor contains one or more nitroxyls selected from the group consisting of:

N,N-di-*tert*-butylnitroxide;

N,N-di-*tert*-amylnitroxide;

N-*tert*-butyl-2-methyl-1-phenyl-propylnitroxide;

10 N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropylnitroxide;

2,2,6,6-tetramethyl-piperidinyloxy;

4-amino-2,2,6,6-tetramethyl-piperidinyloxy;

4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-oxo-2,2,6,6-tetramethyl-piperidinyloxy;

15 4-dimethylamino-2,2,6,6-tetramethyl-piperidinyloxy;

4-ethanoyloxy-2,2,6,6-tetramethyl-piperidinyloxy;

2,2,5,5-tetramethylpyrrolidinyloxy;

3-amino-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,4,4-tetramethyl-1-oxa-3-azacyclopentyl-3-oxy;

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- 2,2,4,4-tetramethyl-1-oxa-3-pyrrolinyl-1-oxy-3-carboxylic acid;
- 2,2,3,3,5,5,6,6-octamethyl-1,4-diazacyclohexyl-1,4-dioxy;
- 4-bromo-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-chloro-2,2,6,6-tetramethyl-piperidinyloxy;
- 5 4-iodo-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-fluoro-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-cyano-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-carboxy-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-carbomethoxy-2,2,6,6-tetramethyl-piperidinyloxy;
- 10 4-carbethoxy-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-cyano-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-methyl-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-carbethoxy-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;
- 4-hydroxy-4-(1-hydroxypropyl)-2,2,6,6-tetramethyl-piperidinyloxy;
- 15 4-methyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
- 4-carboxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
- 4-carbomethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
- 4-carbethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
- 4-amino-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

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4-amido-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

3,4-diketo-2,2,5,5-tetramethylpyrrolidinyloxy;

3-keto-4-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;

3-keto-4-benzylidine-2,2,5,5-tetramethylpyrrolidinyloxy;

5 3-keto-4,4-dibromo-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,3,3,5,5-hexamethylpyrrolidinyloxy;

3-carboximido-2,2,5,5-tetramethylpyrrolidinyloxy;

3-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;

3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

10 3-cyano-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

3-carbomethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

3-carbethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,5,5-tetramethyl-3-carboxamido-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-amino-2,5-dihydropyrrole-1-oxyl;

15 2,2,5,5-tetramethyl-3-carbethoxy-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-cyano-2,5-dihydropyrrole-1-oxyl;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate;

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bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)n-butylmalonate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)phthalate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)isophthalate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)terephthalate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)hexahydroterephthalate;

N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide;

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-caprolactam;

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-dodecylsuccinimide;

2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine; and

4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one).

76. Method of claim 44 wherein said monomers contain impurities from the monomer production and/or purification processes.

77. Method of claim 76 wherein the impurities include polymer formed during the production and/or purification processes.

78. Method of claim 77 wherein the polymer formed during the production and/or purification processes is soluble in the monomer stream.

79. Method of claim 77 wherein the polymer formed during the production and/or purification processes is insoluble in the monomer stream.

5 80. Method of claim 44 wherein said monomers are undergoing purification by distillation.

81. Method of claim 80 wherein the distillation process occurs at pressures less than 760 mm Hg.

10 82. Method of claim 80 wherein the distillation process is a continuous process.

83. Method of claim 80 wherein the equipment in which the distillation process occurs contains polymer.

15 84. Method of claim 83 wherein the polymer was formed during the monomer's production and/or purification processes.

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85. Method of claim 83 wherein the polymer is not dissolved in the monomer stream.

86. Method of claim 80 wherein said monomers contain impurities from the monomer production and/or purification processes.

87. Method of claim 86 wherein the impurities include polymer formed during the production and/or purification processes.

88. Method of claim 87 wherein the polymer formed during the production and/or purification processes is soluble in the monomer stream.

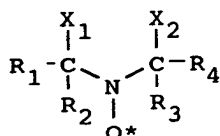
89. Method of claim 87 wherein the polymer formed during the production and/or purification processes is insoluble in the monomer stream.

15

90. A composition comprising:

A) at least one first inhibitor that is a hydrogen donor or an electron acceptor and

B) at least one second inhibitor having the following structural formula:



wherein

5 R_1 and R_4 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl;

R_2 and R_3 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl; and

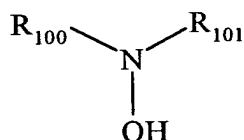
X_1 and X_2

10 (1) are independently selected from the group consisting of halogen, cyano, amido, -S- C_6H_5 , carbonyl, alkenyl, alkyl of 1 to 15 carbon atoms, COOR_7 , -S-COR₇, and -OCOR₇, wherein R_7 is alkyl or aryl, or

(2) taken together, form a ring structure with the nitrogen.

15 91. The composition of claim 90 wherein the first inhibitor is a hydrogen donor.

92. The composition of claim 91 wherein the first inhibitor is of the structure

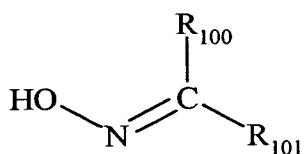


wherein

R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , $COOR_{102}$, $CONR_{102}R_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

93. The composition of claim 91 wherein the first inhibitor is of the structure



wherein

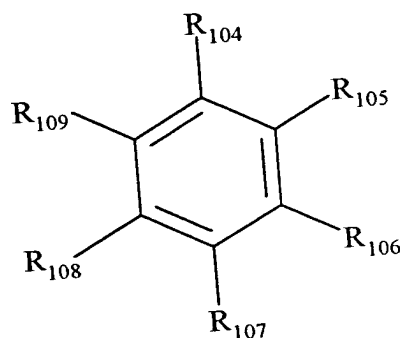
R_{100} and R_{101} are independently selected from the group consisting of hydrogen, alkyl, alkylidene, benzylidene, aryl, benzyl, COR_{102} , $COOR_{102}$, $CONR_{102}R_{103}$, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{100} and R_{101} can be taken together to form a ring structure of five to seven members; and

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R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

5

94. The composition of claim 91 wherein the first inhibitor is of the structure



10

wherein

R_{104} , R_{105} , R_{106} , R_{107} , R_{108} , and R_{109} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members, provided that at least one of R_{104} , R_{105} , R_{106} , R_{107} , R_{108} , and R_{109} is OH or NHR_{110} ;

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} , or R_{110} and R_{111} can be taken together to form

20

a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

95. The composition of claim 94 wherein R_{104} is OH.

96. The composition of claim 95 wherein R_{107} is OH.

97. The composition of claim 95 wherein R_{105} is OH.

98. The composition of claim 95 wherein at least one of R_{105} and R_{107} is NO_2 .

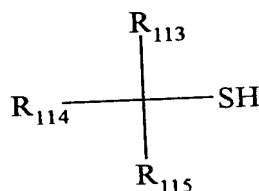
99. The composition of claim 95 wherein at least one of R_{105} and R_{107} is NO.

100. The composition of claim 94 wherein R_{104} is NHR_{110} and at least one of R_{105} and R_{107} is NO_2 .

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101. The composition of claim 94 wherein R_{104} is NHR_{110} , R_{107} is $NR_{110}R_{111}$, and R_{111} is phenyl.

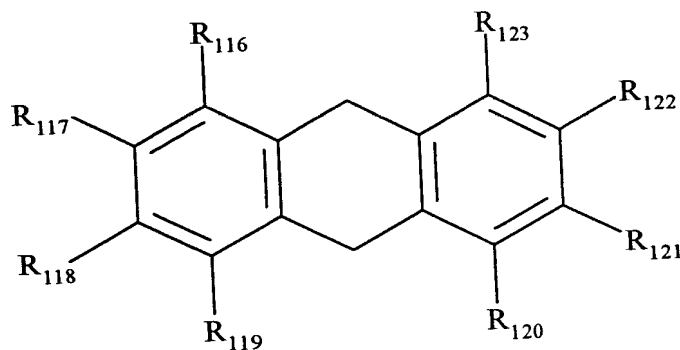
102. The composition of claim 91 wherein the first inhibitor is of the structure



wherein

R_{113} , R_{114} , and R_{115} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, and heterocyclic moieties.

103. The composition of claim 91 wherein the first inhibitor is of the structure



wherein

R_{116} , R_{117} , R_{118} , R_{119} , R_{120} , R_{121} , R_{122} , and R_{123} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or any two adjacent groups can be taken together to form ring structure(s) of five to seven members;

5

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

15

104. The composition of claim 91 wherein the first inhibitor is selected from the group consisting of diethylhydroxylamine, cyclohexanoneoxime, dibenzylhydroxylamine, 2,4-dinitro-6-sec-butylphenol, N-phenyl-N'-(1,4-dimethylpentyl)-para-phenylenediamine, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone, methylhydroquinone, 4-t-butylhydroquinone, 4-t-butylcatechol, octanethiol, 2,6-di-t-butyl-4-ethylphenol/Cu(I)naphthenate, dihydroanthracene, N-t-butyl-2-benzothiazole-sulfenamide, and N-methyl-4-nitroaniline.

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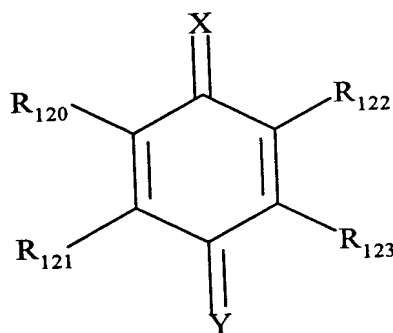
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105. The composition of claim 91 wherein a transition metal is added.

106. The composition of claim 105 wherein the transition metal is copper.

107. The composition of claim 90 wherein the first inhibitor is an electron acceptor.

108. The composition of claim 107 wherein the first inhibitor is of the structure



wherein

X and Y are independently selected from the group consisting of oxygen, NR_{110} , and

$\text{CR}_{124}\text{R}_{125}$;

R_{120} , R_{121} , R_{122} , and R_{123} are independently selected from the group consisting of

hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl,

OR_{110} , $\text{NR}_{110}\text{R}_{111}$, SR_{110} , NO , NO_2 , CN , COR_{112} , and halogen, or R_{120} and R_{121}

can be taken together and/or R_{122} and R_{123} can be taken together to form one or

two ring structures, respectively, either of which can be of five to seven

members;

R_{124} and R_{125} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} ,

$NR_{110}R_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , halogen, and/or can be taken together

to form a ring structure of five to seven members,

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents

are C, O, N, S, or P, and COR_{102} , or R_{110} and R_{111} can be taken together to form

a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $NR_{102}R_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the

substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form

a ring structure of five to seven members.

109. The composition of claim 108 wherein X and Y are oxygen.

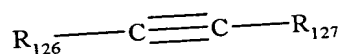
110. The composition of claim 108 wherein X is oxygen and Y is $CR_{124}R_{125}$.

111. The composition of claim 108 wherein X is oxygen and Y is NR_{110} .

112. The composition of claim 108 wherein X and Y are NR_{110} .

113. The composition of claim 112 wherein X is NR_{110} and Y is $\text{CR}_{124}\text{R}_{125}$.

114. The composition of claim 107 wherein the inhibitor is of the structure



wherein

R_{126} and R_{127} are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, heterocyclic, substituted alkyl, substituted aryl, OR_{110} , $\text{NR}_{110}\text{R}_{111}$, SR_{110} , NO_2 , NO , CN , COR_{112} , and halogen;

R_{110} and R_{111} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, substituted alkyl or aryl where the substituents are C, O, N, S, or P, and COR_{102} or R_{110} and R_{111} can be taken together to form a ring structure of five to seven members;

R_{112} is R_{102} , OR_{102} , or $\text{NR}_{102}\text{R}_{103}$; and

R_{102} and R_{103} are independently selected from the group consisting of hydrogen, alkyl, aryl, benzyl, cyclic, heterocyclic, and substituted alkyl or aryl where the substituents are C, O, N, S, or P, or R_{102} and R_{103} can be taken together to form a ring structure of five to seven members.

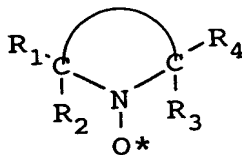
115. The composition of claim 107 wherein the first inhibitor is selected from the group consisting of phenylacetylene, 2,5-di-t-butyl-1,4-benzoquinone, 2,6-di-t-butyl-1,4-benzoquinone, 1,4-benzoquinone, 2-methylantraquinone, 1,4-naphthoquinone, 2,6-di-t-butyl-4-(phenylmethylene)-2,5-cyclohexadiene-1-one, 2,6-di-t-butyl-4-(phenylimino)-2,5-cyclohexadiene-1-one, and ethyl 3,4-bis-(3,5-di-t-butyl-4-one-2,5-cyclohexadienylidene)-hexane-1,6-dioate.

116. The composition of claim 107 wherein a transition metal is added.

117. The composition of claim 116 wherein the transition metal is copper.

118. The composition of claim 90 wherein the first inhibitor is a blend of a hydrogen donor and an electron acceptor.

119. The composition of claim 90 wherein the second inhibitor is of the structure



wherein R_1 and R_4 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_2 and R_3 are independently selected from

the group consisting of alkyl and heteroatom-substituted alkyl, and the



portion represents the atoms necessary to form a five-, six-, or seven-membered
heterocyclic ring.

120. The composition of claim 90 wherein the second inhibitor is a blend of two nitroxyls.

121. The composition of claim 119 wherein the second inhibitor contains one or more nitroxyls selected from the group consisting of:

N,N-di-*tert*-butylnitroxide;

N,N-di-*tert*-amylnitroxide;

N-*tert*-butyl-2-methyl-1-phenyl-propylnitroxide;

N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropylnitroxide;

2,2,6,6-tetramethyl-piperidinyloxy;

4-amino-2,2,6,6-tetramethyl-piperidinyloxy;

4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-oxo-2,2,6,6-tetramethyl-piperidinyloxy;

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4-dimethylamino-2,2,6,6-tetramethyl-piperidinyloxy;

4-ethanoyloxy-2,2,6,6-tetramethyl-piperidinyloxy;

2,2,5,5-tetramethylpyrrolidinyloxy;

3-amino-2,2,5,5-tetramethylpyrrolidinyloxy;

5 2,2,4,4-tetramethyl-1-oxa-3-azacyclopentyl-3-oxy;

2,2,4,4-tetramethyl-1-oxa-3-pyrrolinyl-1-oxy-3-carboxylic acid;

2,2,3,3,5,5,6,6-octamethyl-1,4-diazacyclohexyl-1,4-dioxy;

4-bromo-2,2,6,6-tetramethyl-piperidinyloxy;

4-chloro-2,2,6,6-tetramethyl-piperidinyloxy;

10 4-iodo-2,2,6,6-tetramethyl-piperidinyloxy;

4-fluoro-2,2,6,6-tetramethyl-piperidinyloxy;

4-cyano-2,2,6,6-tetramethyl-piperidinyloxy;

4-carboxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-carbomethoxy-2,2,6,6-tetramethyl-piperidinyloxy;

15 4-carbethoxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-cyano-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-methyl-2,2,6,6-tetramethyl-piperidinyloxy;

4-carbethoxy-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-hydroxy-4-(1-hydroxypropyl)-2,2,6,6-tetramethyl-piperidinyloxy;

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- 4-methyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
4-carboxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
4-carbomethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
4-carbethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
5 4-amino-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
4-amido-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;
3,4-diketo-2,2,5,5-tetramethylpyrrolidinyloxy;
3-keto-4-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;
3-keto-4-benzylidene-2,2,5,5-tetramethylpyrrolidinyloxy;
10 3-keto-4,4-dibromo-2,2,5,5-tetramethylpyrrolidinyloxy;
2,2,3,3,5,5-hexamethylpyrrolidinyloxy;
3-carboximido-2,2,5,5-tetramethylpyrrolidinyloxy;
3-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;
3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;
15 3-cyano-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;
3-carbomethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;
3-carbethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;
2,2,5,5-tetramethyl-3-carboxamido-2,5-dihydropyrrole-1-oxyl;
2,2,5,5-tetramethyl-3-amino-2,5-dihydropyrrole-1-oxyl;

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2,2,5,5-tetramethyl-3-carbethoxy-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-cyano-2,5-dihydropyrrole-1-oxyl;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate;

5 bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)n-butylmalonate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)phthalate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)isophthalate;

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)terephthalate;

10 bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)hexahydroterephthalate;

N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide;

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-caprolactam;

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-dodecylsuccinimide;

2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine; and

15 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one).